

## Paper and a Method of Making Paper

The present invention relates to paper and methods of making paper and more particularly, to compositions, pulp suspensions and processing to provide for white paper production.

5 Paper is made from a pulp stock or suspension incorporating a number of ingredients but principally fibres in order to provide through appropriate processing sheets or rolls of paper. The fibres in the paper stock can be obtained from a number of sources but are principally obtained from tree sources such as cellulose fibre. The tree fibres are appropriately macerated  
10 in order to provide the fibres required. Unfortunately, fibres are biologically active and inherently slightly mis-coloured such that in attempting to form good quality white paper it is necessary to bleach that paper. It is also a typical requirement to add a so-called optical brightness agent (OBA) which is an ultra-violet dye which upon exposure to light radiates a bright white light  
15 hue giving the impression of a pure white colour and masks any potential yellow white in the fibres after bleaching. Unfortunately, OBA materials are relatively expensive and so care must be taken with the proportion of such OBA material added to the pulp stock for economic reasons. It will also be understood that the production of paper inherently generates large volumes of  
20 waste water and any contamination and in particular toxic or environmentally impacting agents such as OBA should be limited in that waste water.

There are a number of OBA and FWA additives available from suppliers such as Bayer AG and from Ciba under their product names Tinopal VP, ABPZ and SPP. Generally, the OBA and FWA additives are fluorescent  
25 dyes. Typically, these fluorescent dyes include sulphonated stilbene molecules.

Previous additives to thick pulp stock include sodium hypochlorite (bleach) and chlorine. Hypochlorite bleaches the fibres in the pulp stock but the pH level dramatically increases and some bi-products of the bleaching

process are deemed environmentally unfriendly. Furthermore, sodium hypochlorite is a slow acting additive at low temperatures and residuals from the bleaching process may have adverse effects on other paper making additives.

- 5           Hydrogen peroxide is also used for bleaching paper stock but normally at elevated temperatures and with the hydrogen peroxide in a concentration of at least 50% in the stock. In such circumstances, hydrogen peroxide bleaching of paper stock is very hazardous. It is also known to provide hydrogen peroxide in combination with polydadmac in order to act as a  
10       bleaching agent. However, such a combination only provides a limited increase in paper stock brightness.

- Hydrogen sulphite can also be added to paper stock and is a reductive "bleach" in comparison with the sodium hypochlorite and hydrogen peroxide oxidising bleach process. Hydrogen sulphite is generally supplied as a  
15       powder requiring on-site preparation by dissolving the powder to form the additive solution. If wetted, hydrosulphite releases sulphur dioxide gas with potential dangerous consequences. Hydrosulphite is also difficult to handle as a liquid and must be kept dry in order to avoid the sulphur dioxide gas release problem.

- 20           In view of the above, it will be appreciated that current additives to bleach paper stock are inconvenient or even dangerous to use whilst they have limited effect upon the brightness achieved or the proportion of fluorescent whitening agent (FWA) or, more commonly, optical brightening agent (OBA) which is required to achieve the desired paper brightness and  
25       tone.

          In accordance with the present invention there is provided a composition for cellulose suspensions, the composition comprising peroxyacetic acid or peracetic acid and hydrogen peroxide in sufficient relative concentration to reduce the necessary proportion of fluorescent

whiting agent (FWA) or optical brightening agent (OBA) required to achieve the desired brightness in finished paper or paper board products formed from the cellulose suspension.

Alternatively, in accordance with the present invention there is provided  
5 a suspension for paper or paper board making, the suspension including an additive comprising a peroxyacetic and/or peracetic acid and hydrogen peroxide composition added to a cellulose fibre stock after pulping.

Preferably, the composition comprises at least 12.5 weight percent peroxyacetic acid and/or peracetic acid. Preferably, the composition includes  
10 a polyamine or other cationic materials to facilitate reaction of the peroxyacetic acid and/or peracetic acid with cellulose fibres. Typically, the composition comprises 15% peroxyacetic acid and 14% hydrogen peroxide. Typically, the polyamine or other cationic materials are added in the range of 1 – 20% by volume to the composition.

15 Further in accordance with the present invention there is provided a process for preparing a suspension comprising forming a cellulose fibre pulp suspension and adding a composition of peroxyacetic acid and/or peracetic acid and hydrogen peroxide before any other additives are added to the suspension.

20 Typically, a polyamine or other cationic material is added in the range of 1 – 20% by volume to the composition in the suspension.

Preferably, the composition is added in the process when the pulp suspension has a consistency of at least 2% or greater of cellulose fibres. Typically, if the composition has a concentration of at least 12.5%  
25 peroxyacetic acid or peracetic acid, then the composition is added to the suspension in the proportion 50 millilitres of composition per gross tonne of cellulose fibre or dry solids in the suspension. Alternately, there is preferably 7 litres of composition to 1 tonne of pulp suspension formed from cellulose

fibres and water. Further alternatively, in the order of 50g to 7kg of composition per tonne of gross paper is initially added then allowed to react for a pre-determined process time and a further 50g to 7kg of composition added per tonne of gross paper for final preparation.

- 5           Typically, the process allows for a process time of at least 30 minutes between adding the composition to the pulp suspension and adding any further additives such as FWA or OBA.

Typically, a polyamine or other cationic material is added in the range of 1 – 20% by volume to the composition during the process.

- 10           Possibly, the process provides for batch processing of vats of pulp suspension or continuous processing.

- Typically, pulp suspension is calibrated at the end of the process time to determine whether the composition has been effective against a desired brightness and further composition added, if required, and/or a further period of processing time allowed. Generally, FWA and OBA is added to the pulp suspension at the end of the processing time or at least prior to paper or paper board forming from the pulp suspension.
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Embodiments of the present invention will now be described by way of example only.

- 20           The process for forming paper is well known. Typically, fibrous materials, chiefly of a vegetable origin are mixed with a large quantity of water and shredded into very fine fibres. The suspension or pulp stock typically includes additives such as size, OBA and filler in order to render a special property to the paper.

- 25           The fibrous material is generally obtained from trees, grasses, bamboo and cotton. There are numerous mechanical, chemical and bio-chemical

processes for pulping the fibrous material to an appropriately thick stock or stuff for paper or paper board formation. Various grades of paper are provided and typically comprise various combinations of fibrous vegetable material as described previously along with other fibres such as hemp, linen, wool, asbestos, slag wool, glass fibres and synthetic fibres along with fillers, size and other additives in order to achieve a desired paper quality.

The present invention principally relates to providing relatively high quality white paper and paper board. To achieve such high quality paper a so-called fluorescent whitening agent or FWA is added. Such fluorescent whitening agents are also known as optical brightening agents (OBA). In short, such FWA or OBA materials fluoresce on exposure to light in order that the paper incorporating such agents appears brighter and therefore whiter. FWA and OBA are relatively expensive additives in a typical paper combination and so there are strong economic reasons for limiting their proportion of the combination in terms of a weight percentage. It will also be understood that FWA or OBA materials are considered unfriendly environmental agents such that waste water from the paper making process must be appropriately treated to remove such FWA or OBA agents prior to release.

As with all vegetable matter the fibres used with regard to paper making will tend to be discoloured relative to the desired whiteness as well as biologically active. In such circumstances, as indicated previously, it is known to bleach suspensions or pulp stock in order to render the fibres of a whiter surface complexion as well as reduce biological activity which may itself discolour the fibres as the paper ages. Traditional bleaching methods, whether they be oxidising or reducing, create their own inherent problems with respect to residuals left in the paper after forming, processing dangers and waste water contamination.

The present invention utilises a composition added to the pulp suspension prior to other additives. This composition comprises a mixture of

peroxyacetic acid or peracetic acid with hydrogen peroxide. One source of such composition is Crosmill Limited of Crosmill House, Dragons Lane, Moston, Sandbach, Cheshire, United Kingdom under their product name. Crosmill Millicide PH120 which comprises a solution including 15%  
5 peroxyacetic acid or peracetic acid with a similar proportion of hydrogen peroxide. With such a composition, it has been found that above a greater than 2.5 weight percent concentration in the pulp suspension the composition provides a sufficiently active concentration to render the fibres and more particularly the suspension stock more receptive to FWA or OBW additives  
10 later. Typically, the pulp suspension or stock will have a so-called thick consistency of upwards of 2 weight percent cellulose solids or fibres in the suspension. Generally, the composition must be given an effective free period of process time during which it can actively process the suspension. With the composition concentration of peroxyacetic acid with hydrogen  
15 peroxide described above it has been found that a process time of 30 minutes from addition of the composition to the suspension pulp is normally appropriate. The composition and in particular the peroxyacetic acid and/or peracetic acid conditions the cellulose fibre surface to render it more receptive to association with the FWA or OBA material later.

20 Clearly, it is still normally necessary to add FWA or OBA materials to the suspension stock to achieve the desired whiteness in eventual paper or paper board product. Nevertheless, with the suspension stock processed in accordance with the present invention, the fibres and the suspension are more receptive to such FWA or OBA materials and a significantly lower  
25 proportion of such FWA or OBA materials is required to achieve the desired brightness in the finished product. Normally, the present composition used in the pulp suspension and paper making process will halve the necessary amount of FWA or OBA which needs to be added to achieve a desired whiteness and brightness.

As indicated, in order to be effective, the proportion of fibre solids in the suspension should be at least 2% by weight such that the composition in accordance with the present invention is able to efficiently process these fibres. A more diluted consistency will render the amount of composition which is required to be effective in the suspension to be significantly increased due to inherent reduction in fibre to composition association. The composition in accordance with the present invention itself will be relatively costly and therefore the more composition required to process the pulp suspension the less cost effective the process will be. Although excess composition may be recovered from waste water during later stages of the paper making process, such recovery may be expensive and inherently some composite will be lost through each use cycle.

As the present composition acts upon the thick suspension of cellulose fibres used, in accordance with known techniques for paper making and paper board making, it will be understood that the fibres themselves will have an increased whiteness or brightness. In some circumstances, it may not be necessary to add FWA or OBA materials to achieve the desired brightness in the finished paper or paper board product, particularly if white fillers or additives such as chalk, gypsum or china clay are included.

In accordance with an example of the process of the present invention, a suspension pulp will be formed in accordance with conventional techniques to a consistency of at least 2% by weight of cellulose fibres, a composition of at least 12.5% peroxyacetic acid with proportionate amount of hydrogen peroxide in a liquid form will then be added in the proportion of 50 millilitres of such composition to each gross metric tonne of cellulose fibres/solids or 7 litres of composition per metric tonne of pulp suspension. Typically, individual vats of suspension pulp will be processed such that the appropriate process time, normally 30 minutes, can be applied to each vat of pulp suspension in accordance with the present invention. Alternatively, through appropriate pipework and/or holding tanks the suspension pulp can be continuously

processed such that the pulp is at least solely exposed to the composition for the necessary process time in accordance with the present invention between additional of the composition to the suspension and addition of any further additives to that suspension.

5           In order to further improve performance but possibly with the increased cost and recovery problems, the proportion of composition may be raised such that composition is added to the suspension pulp with a proportion in the range of 50g to 7kg of composition per tonne of gross paper. The suspension  
10       pulp is then allowed to act during a process time period and then a further volume of composition added in the range of 50g to 7kg per tonne of gross paper. In such circumstances, there is a significant increase in brightness lift to the eventual paper quality. For example, if previously there was a one point base paper brightness lift then by these additions, the brightness lift is increased to two points in base brightness lift.

15           In order to further enhance the process in accordance with the present invention, the polyamine or other cationic material can be added to the peracetic acid or composition. The polyamide or other cationic material will be added in the range of 1 – 20% by volume to the composition in order to  
20       further promote the reaction processes performed by the composition in order to prepare the paper pulp suspension for receipt of an optical brightness agent (OBA). In such circumstances, the proportional improvement in optical brightness relative the amount of OBA added is significantly increased. Thus, better quality paper can be produced at a reduced cost or paper quality maintained with lower OBA content.

25           At the end of the composition processing time, it is found that the effect of the composition on the suspension will be to increase the brightness of that pulp and the resultant finished paper is brighter than if the composition had not been added. Generally, there is an increased brightness in the range of 1 to 3 points dependent upon the type of fibre and initial brightness of the pulp.  
30       This increased brightness is substantially and proportionately the same with



or without the eventual addition of FWA or OBA materials in the finished paper in accordance with normal practice. There is also a corresponding increase in the whiteness and "L" values of the suspension pulp or finished paper sheet. The "L" value relating to brightness within 100 = pure white and 0 = black. The colour of the suspension pulp/finished paper also changes. Typically, the finished paper becomes less yellow and bluer, the "b" value is ratio between blue and yellow and is less positive; this is an advantage as less dye material may be needed with significant economic savings whilst promoting improved brightness in the paper itself. The "a" value (red to green ratio) of the finished paper sheet does not change very much; if there is any change in this "a" value it is a shift from green to red but is normally only of a slight nature.

As indicated above, after the processed time other additives will normally be incorporated into the suspension pulp prior to final paper forming and processing. Generally, before such further additives are incorporated into the suspension pulp there will be a calibration test in order to determine the specific whiteness, brightness and other control values used to determine pulp suspension quality. It will be understood that as with all natural products, vegetable fibres and in particular cellulose solids and fibres obtained from tree matter will vary with environment, age, season and source. Thus, the present composition may have significantly different, or at least marginally different, effects upon different batches of suspension pulp. Thus, if the "processed" suspension pulp has not met the desired brightness or whiteness values for onward processing then further FWA or OBA materials may be needed or the particular batch of suspension pulp allowed to resume further processing by the composition or, if necessary, further composition added to the suspension pulp to increase the concentration of the composition in that suspension. In any event, it will be understood that temperature along with other factors such as agitation will significantly effect the necessary processing time to achieve the desired brightness or whiteness in the suspension pulp and subsequent finished paper product. Operational temperatures will be in the range 5 to

50°C but the colder temperature the longer time necessary processing time for reaction.

The present composition and resultant suspension pulp and process allow a paper manufacturer to either maintain finished sheet brightness and colour at a low cost due to less dye and FWA materials added or maintain  
5 current dye and FWA material content in the finished paper sheet but produce a higher quality product with higher whiteness and brightness. Furthermore, a paper manufacturer could specify a higher quality paper by use of the present composition whilst at the same time reducing cost through lower dye and  
10 FWA additive components specified for that paper.

It will be appreciated that the present composition effectively chemically conditions the pulp suspension. Thus, in order to increase and facilitate the operational efficiency cationic materials may be added to the composition or separately during the process. The free radicals provided by  
15 disassociation of such cationic material will promote processing of the suspension pulp by the composition either in terms of rate or effectiveness. It will be understood that care will be necessary with regard to the choice of cationic material used such that the cationic material is either dissolved in the water or composition and there is little residual solid cationic material retained  
20 in the finished paper with a potential reduction in the quality of that paper.

Whilst endeavouring in the foregoing specification to draw attention to those features of the invention believed to be of particular importance it should be understood that the Applicant claims protection in respect of any patentable feature or combination of features hereinbefore referred to whether  
25 or not particular emphasis has been placed thereon.